ORGANIC GEOCHEMICAL ANALYSIS OF SHALY FACIES FROM TWO WELLS WITHIN ANAMBRA BASIN, SOUTHEASTERN NIGERIA.

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ABSTRACT

Organic geochemical analysis of two selected wells penetrating shale facies of the Anambra basin was conducted with the view of evaluating the section in terms of quantity and quality of organic matter, genetic potential, organic matter type, thermal maturity as well as determining the type of hydrocarbon that could be generated. Geochemical parameters such as Total Organic Carbon (TOC), S1 (representing free and adsorbed hydrocarbons present), S2 (representing hydrocarbons generated directly from the kerogen), S3 (carbon dioxide CO_2 present) and maximum temperature (T_{max}) as well as Hydrogen Index (HI), Oxygen Index (OI), Production Index (PI) and Genetic Potential (GP) were derived and calculated from the pyrolysis data. Result indicated that Well 1 samples have an average TOC of 1.21 wt % which is considered good in organic matter quantity and fair in quality, while Well 2 samples are organically lean, poor in quantity and quality with average TOC value of 0.15 wt %. The Genetic Potential (GP) expressed as (S1+S2) for Well 1 and Well 2 averages 2.03 and 0.68 mg HC/g respectively, indicating, a poor generational potential. The HI, OI and S2/S3 values of Well 1 samples are 146.56 mg HC/g, 226.78 mg HC/g and 0.86 respectively which on plots suggest the kerogen as type IV although few samples fall within the type III area. This contrasts with Well 2 samples having HI, OI and S2/S3 values as 343.67 mg HC/g, 276.78 mg HC/g and 1.26 respectively. Thus making the kerogen type to be interpreted as type III. Judging from T_{max} (average of 441.67^0C for Well 1 and 470.44^0C for Well 2) and PI (average of 0.13 for Well 1 and 0.24 for Well 2) values, Well 1 samples are within the oil generating window whereas Well 2 samples are overmatured generating dry gas. Deductions from the result of geochemical analysis, depicts that the kerogen of Well 1 samples will generate oil while that of Well 2 samples have propensity to generate dry gas.

1 INTRODUCTION

The generation of oil and gas from a matured source rock depends on the provenance of the organic matter contained in the sediments. According to (Tissot and Welte, 1984) detailed geochemical analysis of the source rock can provide deep information on the environmental conditions during the time of deposition, the level of thermal maturity and the characteristics of the hydrocarbon that will be generated. Predominantly terrestrially derived organic matter, favour the generation of more gas than oil. Since the minimum concentration of organic carbon necessary for petroleum generation and expulsion is 0.5% (Welte, 1965), any sediment with organic carbon greater than 0.5% is a good petroleum source rock (Hunt, 1975).

Organic carbon in sediment is a function of many factors, which include presence of biogenic material, rapid sedimentation and burial and redox reaction during deposition and diagenesis. The minimum concentration of organic carbon necessary for petroleum generation and expulsion is 0.5% (Welte, 1965 and Espitalie and Bordenave, 1993). Good petroleum source rocks usually contain higher concentration of organic matter (Hunt, 1975).

Theoretically hydrogen is also a great controlling factor in the hydrocarbon generating capacity of sedimentary organic matter. Hydrogen source potential can be explained on the basis of the relative proportion of hydrogen-rich and hydrogen-poor organic components contained in a sedimentary organic matter.

2 LOCATION AND REGIONAL GEOLOGY

The two wells under investigation are located within Anambra Basin, Southeastern Nigeria. The study area covers an area of approximately $218km^{2,}$ on latitudes $5^0 54^I 40.89^{11}$ to $6^0\ 35.09^I$ North and longitudes $7^0\ 6^I\ 32.46^{11}$ to $7^0\ 32.11^I$ East (Fig. 1).

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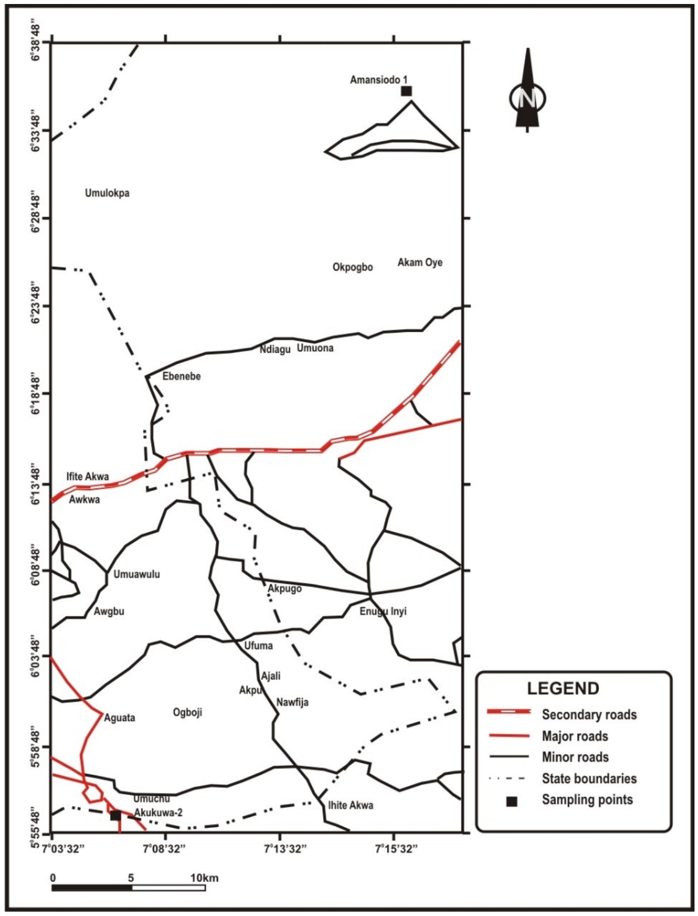

Fig 1: Location map of the study area

Anambra Basin is one of the major Cretaceous depocentres containing over six kilometres of sediments. The discovery of coal in 1900 by Geological Survey Agency of Nigeria has made the basin an object of exploration activities and the good sequence of shales and sandstones, which is a right setting for oil and gas accumulation. The Anambra Basin is a NE-SW trending syncline that is of African Rift System which developed in response to the stretching and subsidence of major crustal blocks during a Lower Cretaceous break-up phase of the Gondwana super-continent (Ogala et al., 2010). The movement was reactivated by further planet activity in Lower Tertiary soon after the intermittent Upper Cretaceous rifting (Ogala et al., 2010).

Sediments deposition started in the basin during the Campanian with Nkporo shale at the bottom, overlain sequentially by Mamu, Ajali, Nsukka, Imo, Ameki and Ogwashi-Asaba Formations (Reyment, 1972; Nwachukwu, 1972; Nwajide *et al.,* 1996, Nwajide, 1990).

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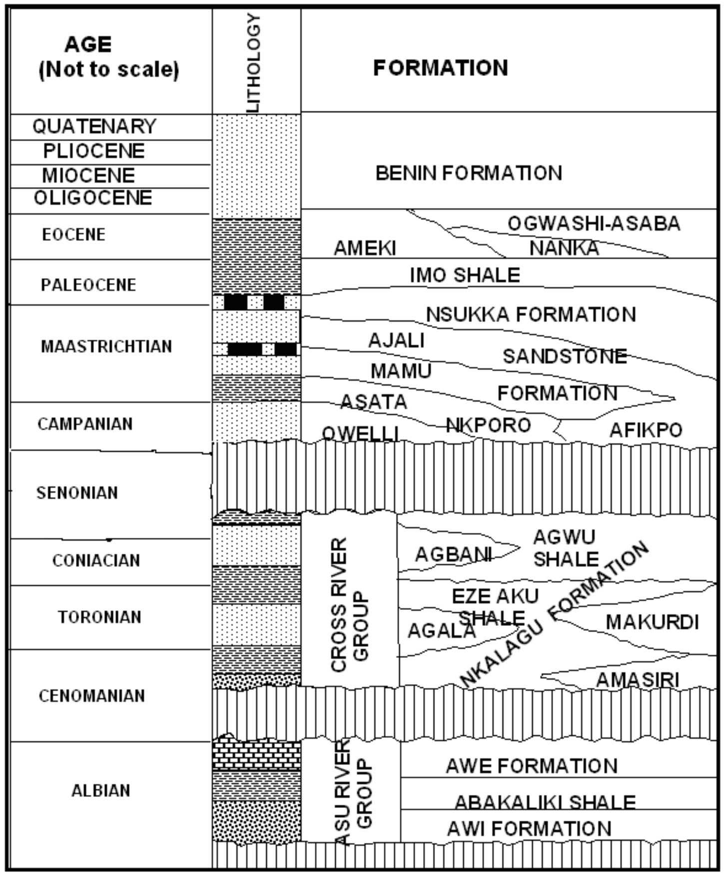

Fig. 2: Regional Stratigraphy of the Anambra Basin (modified from Hoque and Ezepue, 1977).

3 MATERIALS AND METHODS

The well cutting samples for this work was supplied by Nigeria Geological Survey Agency, and it contains shale lithologies of the two wells. The description of lithologies was done by visual inspection using hand lens as well as physical description of the samples. The samples were then subjected to Organic geochemical analysis for the determination of the Total Organic Contents (TOC) and then the Rock Eval pyrolysis.

The sample is pulverized with 20-25g of the crushed to fine powder for 10seconds in a tempered chrome steel mortar of a vibratory disk grinding machine (Fa Siebtechnik). After 10 seconds sample powder was carefully brushed from the grinding set of the mortal and homogenized. The grinding process was repeated for another 10sec after which the powdered sample was manually split. Gram size analysis using Zilas Laser granulometer have shown that the sample is then equivalent to 250mesh or < 63µ (GANZ 1989). 2g of the powdered sample was taken away and repeatedly ground three times 10sec as described above. After the 5th and finally grinding the grain size smaller than 10µ, the other remaining powdered sample that was grounded only (2 x 10 seconds) were stored for organic geochemical analysis

The Total Organic Content (TOC) was determined using LECO CS-224 Analyzer. Rock-Eval pyrolysis method was used to characterize the Kerogen types. TOC, S1, S2, S3 and T_{max} values were gotten from Rock-Eval pyrolysis. Hydrogen Index (HI), Oxygen Index (OI), Genetic Potential (GP), Production Index (PI), Pyrolysed Carbon (PC) and other ratios were calculated from Rock-Eval result. These data sets were used for interpretation.

4 RESULTS AND DISCUSSION

The Rock-Eval pyrolysis data is as presented in the table below. Geochemical parameters, such as HI, OI, GP, etc., have been calculated and are shown in Table 1.

Table 1: Results of Rock- Eval Pyrolysis Analysis, Well-1 and Well-2

TOC = Total Organic Carbon, Tmax = Maximum Temperature, S1= Volatilization of existing Hydrocarbon, S2 = Pyrolysis of Kerogen, S3 = CO_2 and water peak, PI = Production Index, HI = Hydrogen Index and OI = Oxygen Index, PC = Pyrolysed Carbon, GP = Genetic Potential

		Depth (m)	**Lithology**	**TOC(%)**	**T max (0C)**	**HI (S2/TOC)*100**	**OI (S3/TOC)*100**	**S1**	**S2**	**S3**	**GP**	**PI**	**PC**	**S2/S3**
Well I	S-4	1,522	Shale	0.09	426.00	59.00	180.00	0.04	0.05	0.16	0.09	0.43	0.01	0.33
	S-7	1,575	Shale	0.82	443.00	137.00	888.00	0.03	1.12	7.28	1.15	0.03	0.12	0.15
	S-10	1,640	Shale	1.81	440.00	229.00	124.00	0.17	4.14	2.24	4.31	0.04	0.43	1.85
	S-11	1,673	Shale	1.18	437.00	451.00	228.00	0.28	5.32	2.69	5.60	0.05	0.56	1.98
	S-12	1,693	Shale	1.70	438.00	196.00	144.00	0.15	3.33	2.45	3.48	0.04	0.35	1.36
	S-13	1,703	Shale	1.08	450.00	114.00	137.00	0.10	1.23	1.48	1.33	0.08	0.13	0.83
	S-15	1,765	Shale	1.07	471.00	30.00	133.00	0.12	0.32	1.42	0.44	0.27	0.04	0.23
	S-17	1,800	Shale	1.81	442.00	69.00	105.00	0.04	1.25	1.90	1.29	0.03	0.13	0.66
	S-20	1900	Shale	1.34	428.00	34.00	102.00	0.13	0.46	1.37	0.59	0.22	0.06	0.33
Average				**1.21**	**441.67**	**146.56**	**226.78**	**0.12**	**1.91**	**2.33**	**2.03**	**0.13**	**0.20**	**0.86**
Well II	S-5	3,300	Shale	0.04	467.00	370.00	261.00	0.04	0.15	0.10	0.19	0.21	0.02	1.42
	S-6	3,474	Shale	0.10	487.00	393.00	240.00	0.10	0.39	0.24	0.49	0.20	0.05	1.64
	S-8	3,514	Shale	0.10	478.00	293.00	296.00	0.10	0.29	0.30	0.39	0.25	0.04	0.99
	S-9	3,543	Shale	0.20	480.00	395.00	205.00	0.20	0.79	0.41	0.99	0.20	0.10	1.93
	S-11	3,572	Shale	0.26	493.00	421.00	338.00	0.26	1.09	0.88	1.35	0.19	0.14	1.25
	S-13	3,619	Shale	0.10	496.00	401.00	328.00	0.10	0.40	0.33	0.50	0.20	0.05	1.22
	S-14	3,647	Shale	0.20	434.00	340.00	273.00	0.20	0.68	0.55	0.88	0.23	0.09	1.25
	S-15	3,680	Shale	0.15	415.00	114.00	207.00	0.15	0.17	0.31	0.32	0.47	0.03	0.55
	S-16	3,700	Shale	0.21	484.00	366.00	343.00	0.21	0.77	0.72	0.98	0.21	0.10	1.07
Average				**0.15**	**470.44**	**343.67**	**276.78**	**0.15**	**0.53**	**0.43**	**0.68**	**0.24**	**0.07**	**1.26**

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Organic Geochemical Analysis

This shall determine:

Quantity and quality of organic matter

Genetic potential of the source rock

Organic matter type

The thermal maturity of the source rock

The geochemical parameters relevant to determining the above listed items in order to effectively carry out the organic geochemical analysis of the study area include (1) Total organic carbon (TOC) (2) Hydrogen Index (HI), (3) Oxygen Index (OI), (4) Production Index (PI), (5) Maximum Temperature (T-Max) and (6) Genetic Potential (GP) among others which in turn revealed the quantity, quality and thermal maturity of the shale samples.

Quantity and quality of organic matter

The quantity and quality of the source rock organic matter is of utmost important in organic geochemical analysis. This is because, for hydrocarbon accumulation to occur anywhere, organic matter must be present in large (right) quantity. Quantity alone is not sufficient. The type of hydrocarbon (oil, gas, condensates, etc.) that will eventually be produced from a source bed depends mainly on among other factors, the organic matter that produced the kerogen. This refers to the quality of organic matter. Both the quality and the quantity are determined from the values of total organic content (TOC wt %), S1, S2, genetic potential (S1+S2), plots of TOC (wt %) versus S2 and S1 vs TOC (wt %).

The first peak (S1) represents the free and adsorbed hydrocarbons already present, vaporized at 300°C, and the second peak (S2) represents the hydrocarbons generated directly from the kerogen, by thermal cracking at 300-500°C (Espitalie *et al.,* 1977). According to them, S1 is a measure of the bitumen content and S2 is a measure of the insoluble kerogen content measured in (mg HC/g) dry rock. Figure 3 gave a pictorial insight into the quantity (from TOC values) and quality of organic matter.

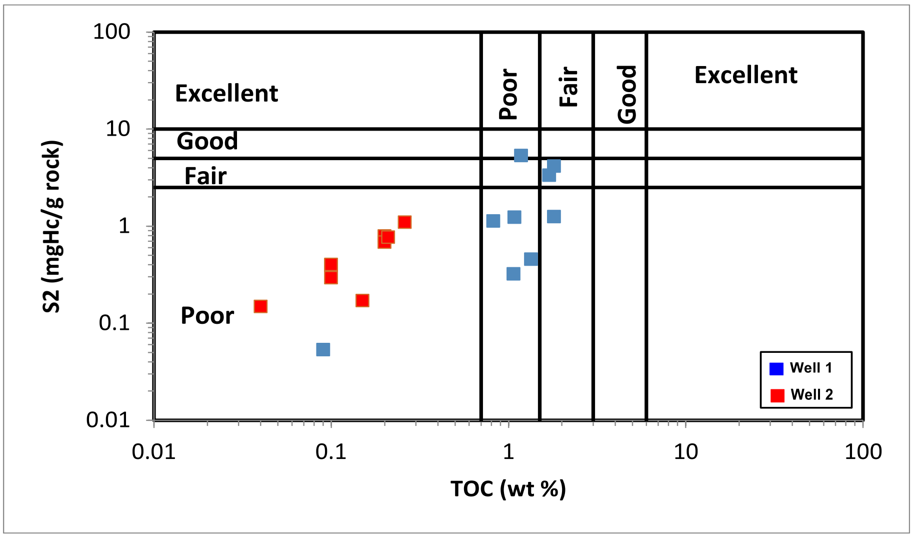


Figure 3: The quality and quantity of the organic matter (modified after Peters and Cassa, 1994)

Peters and Cassa (1994) gave the standard and interpretive range of values for these geochemical parameters as presented in Table 2 below.

Table 2: Geochemical parameters describing TOC, S1 and S2 modified after Peters and Cassa (1994)

Petroleum Potential	TOC (wt. %)	S1 (mg HC/g)	S2 (mg HC/g)
Poor	0-0.5	0-0.5	0-2.5
Fair	0.5-1	0.5-1	2.5-5
Good	1-2	1-2	5-10
Very Good	2-4	2-4	10-20
Excellent	>4	>4	>20

The potential source rocks in this project area are the thick shales of Nkporo Formations. The total organic carbon content of the intervals penetrated by Wells 1 and 2 is presented in table 1. For Well-1 which penetrated Nkporo shales, the TOC ranges from 0.9% to 1.8% (average 1.21%). All the samples have value more than 0.5% which is classified as a good source rock. Also in Well-2, the TOC values ranges from 0.04% to 0.26% (average 0.15%).

For Well 1, S1 value ranges from 0.03 to 0.28 mg HC/g dry rock (average of 0.12 mg HC/g) while those of Well 2 are 0.04 to 0.26 mg HC/g (average of 0.15 mg HC/g). S2 values for Well 1 range from 0.05 to 5.32 mg HC/g (average of 1.91 mg HC/g) while Well 2 has values ranging from 0.55 to 1.09 mg HC/g (average of 0.53 mg HC/g).

According to Peters and Cassa (1994), S2 is a more realistic TOC i.e. its values is more dependable than TOC value because TOC includes ''dead carbon'' incapable of generating petroleum. Therefore, based on the S2 values, the source rock of the study area is considered poor to fair both in quantity and quality.

Genetic Potential of source rock

The generation potential of a source rock could be inferred from the results of pyrolysis analysis. The genetic potential (GP) equals the addition of the values of S1 and S2. Source rocks with a GP <2, from 2 to 5, from 5 to 10 and >10 are considered to have poor, fair, good, and very good generation potential respectively Hunt (1996), El Nady et al (2015).

The genetic potential of (S1+S2) for Well 1 and Well 2 averages 2.03 and 0.68 mg HC/g respectively, indicating, in the overall, a poor generational potential. This means that the organic matter of the source rock lacks the required capacity to generate hydrocarbon of any type.

Table 3: Interpretive values for generation potential (modified after El Nady et al, 2015)

Generation potential, GP (S1+S2)	Interpretation
<2	Poor
2-5	Fair
5-10	Good
>10	Very good

The generating potential of the source rocks under study is generally poor with Well 2 plotting entirely in the poor GP area of fig 4 while only three samples of Well 1 plotted in the fair to good section, others plotted in the poor section as well, thus confirming the low capacity (generating potential) of the source rocks to generate hydrocarbon.

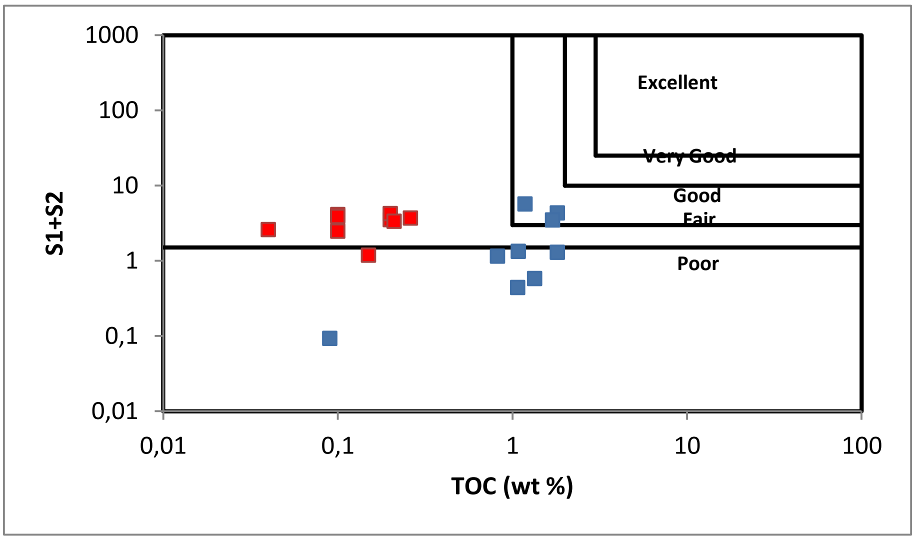


Figure 4: The generation potential of the source rocks in the study area

Organic matter type

The type of organic matter that made up any source rock is of extreme geochemical importance for the accurate prediction of hydrocarbon potential. According to Ali (2013), the type and amount of hydrocarbons produced from a particular kerogen depend on its characteristics, which in turn depend on the type of the organic source material and the digenetic history of the kerogen concerned.

The values of HI and S2/S3 are indicative of the organic matter that made up a source rock.

Table 4: Geochemical parameters describing kerogen type, HI, S2/S3 and fluid expelled modified after Peters and Cassa (1994)

Kerogen Type	HI (mg HC/g TOC	S2/S3	Main Expelled Product at Peak Maturity
I	>600	>15	Oil
II	300-600	10-15	Oil
II/III	200-300	5-10	Mixed oil and gas
III	50-200	1-5	Gas
IV	<50	<1	None

The S2/S3 ratio represents a measure of the amount of hydrocarbons which can be generated from a rock relative to the amount of organic CO_2 released during temperature programming up to 390º C. S2/S3 ratios are considerably lower for Type III kerogen than for Type II and Type I because terrestrially derived organic matter contains substantially more oxygen than the other types of organic matter (Nunez-Betelu and Baceta, 1994). The average S2/S3 ratio for Wells 1 and 2 are 0.86 and 1.26 respectively. This shows that the source rock of the study area is made up of Type III and IV kerogen (fig 5) expelling gas or even nothing.

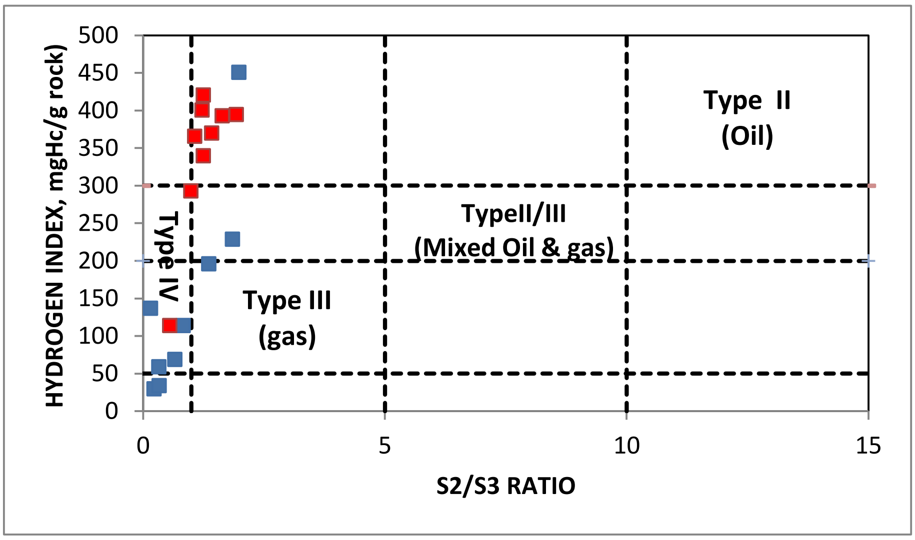
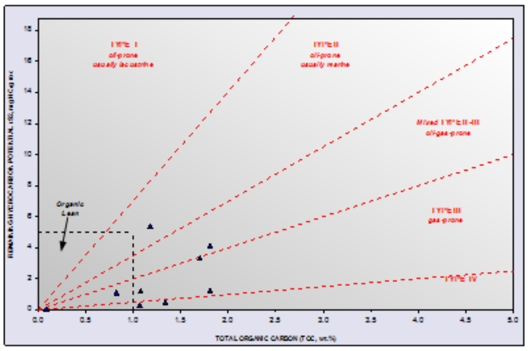


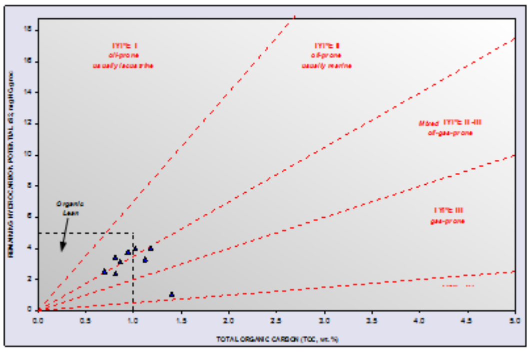
Figure 5: Plot of Hydrogen Index and S2/S3 ratio of samples Well 1 and Well 2 showing kerogen type (quality) and the character of expelled products as defined by Peters and Cassa (1994)

Pyrolysed Carbon (PC) is defined as the ratio (S1 +S2)/10 and is another parameter that gives clue to organic matter type that made up the source rock. Type I kerogen yields PC values of about 80 %, Type II of about 50 %, and Type III between 10-30 % (Nunez-Betelu and Baceta, 1994). The average PC values for the organic matter type for both wells used in this study is 20% for Well 1 and 7% for Well 2. These values again put the Kerogen as Type III and IV.

Majority of the samples of Well 2 samples are organically lean as shown in fig. 6. This notwithstanding, the kerogen type of the samples from both wells are classified as type III and IV (Fig. 6) expelling oil and gas as seen on the modified Van Krevelen plot of HI vs OI (fig. 7).



Classification of Kerogens of Nkporo shale on S_2 (mgHC/g rock) vs TOC (%), Well-1 (Philip *et al.*, 1990).



Classification of Kerogens of Nkporo shale on S_2 (mgHC/g rock) vs TOC (%), Well-2 (Philip *et al.*, 1990).

Figure 6: The classification of the kerogen in Wells 1 and 2 (According to Philip et al., 1990)

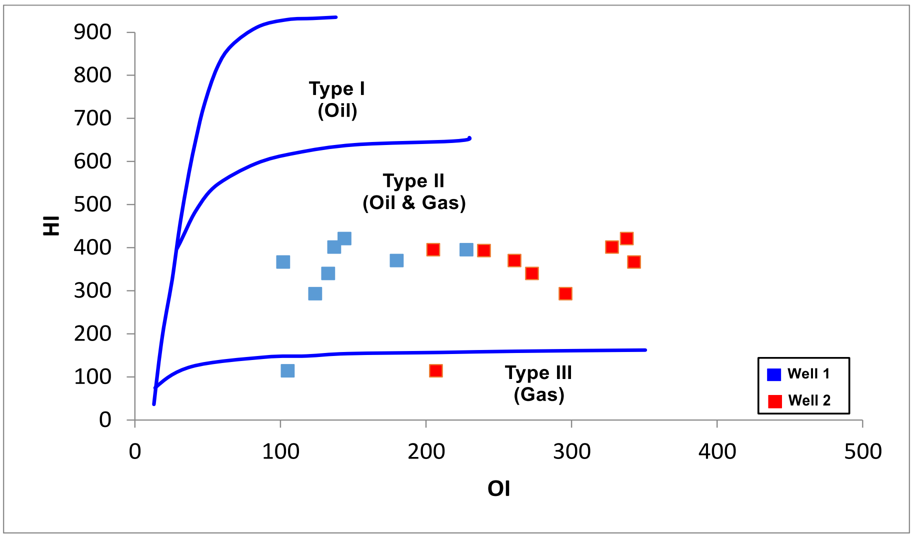


Figure 7: Modified Van Krevelen diagram showing the classification of the kerogen in Wells 1 and 2

Thermal Maturity

Thermal maturity determines the maturity of the organic matter of the source rock i.e. whether or not they have reached petroleum- generating temperature. Its value helps in determining the phase of the hydrocarbon that would be produced.

T_{max}, represents the temperature at which the maximum amount of hydrocarbons degraded

from kerogen are generated and does not represent the actual burial temperature of the rock but rather a relative value of the level of thermal maturity (Nunez-Betelu and Baceta, 1994). Thus, it is used in kerogen maturation rank evaluation (Delvaux et al 1990)

T_{max} measures thermal maturity and corresponds to the Rock-Eval pyrolysis oven temperature (°C) at maximum S2 generation.

The plot between HI and T_{max} (fig 8) put only three samples in the immature zone, majority of Well 1 samples in the oil zone while virtually all except two samples of Well 2 in the gas zone. The implication is that Well 1 samples are within the oil window and can therefore generate oil while Well 2 samples cannot produce any other type of hydrocarbon except gas because they have been ‘overcooked’. Thus, it is inferred that Well 1 samples are thermally matured while Well 2 samples are over matured.

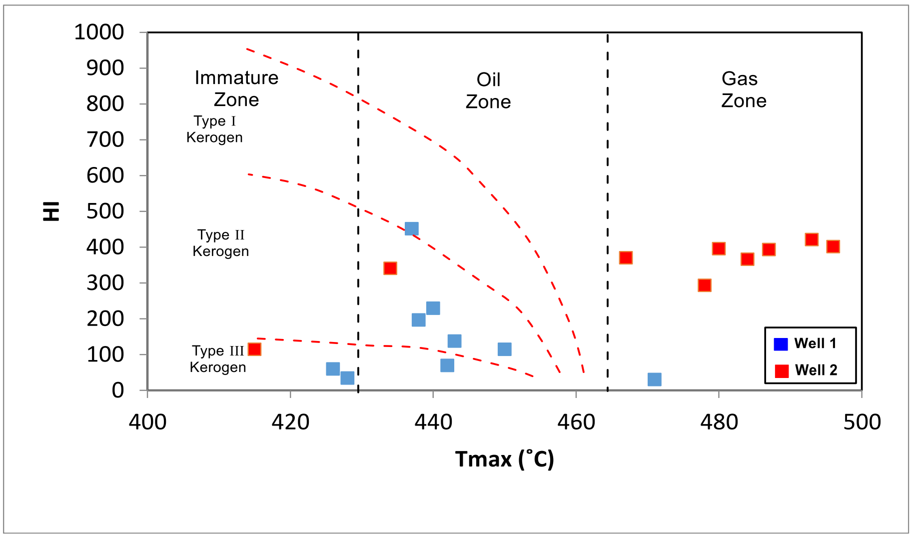


Figure 8: HI vs T_{max} plot indicating thermal maturity of organic matter of Wells 1 and 2

Considering Production Index (PI) vs T_{max} (fig 9), while majority of Well 1 samples fall within the oil window, Well 2 samples fall within the dry gas zone. This corroborated the earlier claim that Well 1 samples are thermally matured and Well 2 samples are over matured.

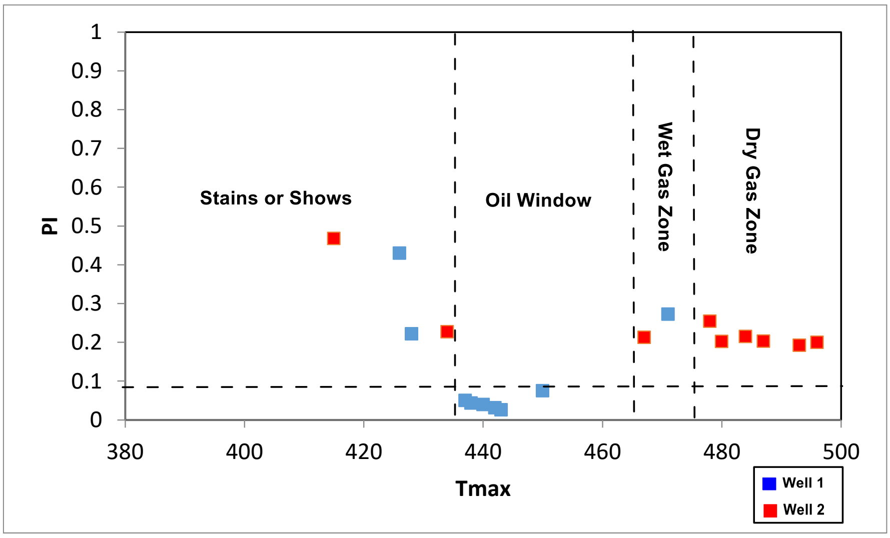


Figure 9: Production Index vs T_{max} showing the level of maturation of samples' organic matter.

CONCLUSION

The organic geochemical analysis for evaluating Nkporo Shale of selected wells in Anambra basin show that:

Well 1: samples have an average TOC of 1.21 wt % which is considered good in organic matter quantity and fair in quality. The HI, OI and S2/S3 plots values put the kerogen types as type IV although about three samples fall within the type III reign. It has fair generating potential. The maturity, based on T_{max}, and PI is with the oil generation window

Well 2: Samples are organically lean, poor in quantity & quality with average TOC value of 0.15 wt% and S2 value 0.53 mgHC/rock. The HI, OI and S2/S3 plots values categorized the kerogen as type III mainly expelling gas, irrespective of the high HI values. The maturity index from T_{max}, and PI values show that the simples are over matured and are with the dry gas zone.

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